

# **REMARKS**

In response to the above-identified Office Action, Applicants amend the application and seek reconsideration thereof. In this response, Applicants amend Claims 1, 3 and 5. Applicants do not cancel or add any claims. Accordingly, Claims 1-8 are pending.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attachment is captioned "Version With Markings To Show Changes Made."

## **I. Claims Rejected Under 35 U.S.C. § 102(e)/103(a)**

The Patent Office rejects Claims 1-4 under 35 U.S.C. 102(e)/103(a) as being anticipated by and alternatively obvious over U.S. Patent No. 6,139,990 to Kubota, et al. ("Kubota"). Applicants respectfully traverse this rejection.

As requested by the Patent Office in the above-identified Office Action, Applicants submit herewith an English translation of Korean Patent Application No. 1998-7854 and a statement that the translation is accurate. Accordingly, Applicants respectfully request withdrawal of the rejection.

The Patent Office rejects Claims 1-8 under 35 U.S.C. 102(e)/103(a) as being anticipated by and alternatively obvious over U.S. Patent No. 5,906,900 to Hayashi, et al. ("Hayashi").

In order to anticipate a claim, the relied upon reference must disclose every limitation of the claim. In order to render a claim obvious, the relied upon reference must teach or suggest every limitation of the claim such that the invention as a whole would have been obvious at the time the invention was made to one skilled in the art. Among other limitations, amended independent Claims 1, 3 and 5 each recite a negative active material having no particular shape. Applicants submit that at least this limitation is neither taught nor suggested by Hayashi.

In maintaining the rejection, the Patent Office relies on Hayashi to show an intensity ratio as recited in Claims 1 and 3. The Patent Office further relies on Hayashi to show coking and graphitizing as recited in Claim 5. In response, Applicants submit that Hayashi fails to teach or suggest that the negative active material has no particular shape.

Specifically, Hayashi states that the composite carbonaceous material disclosed therein may have an optional shape such as a particulate shape or a fibrous shape, with the particulate shape

being preferred (Col. 9, lines 9-13). Hayashi further discloses preferred sizes for a particulate shape and for a fibrous shape, respectively (Col. 9, lines 13-19). Thus, a specific shape (e.g., particulate or fibrous) is required by Hayashi.<sup>NO!</sup>

Therefore, Applicants submit that Hayashi teaches away from Applicants' recited negative active material having no particular shape, which finds support in Applicants' specification on page 9, lines 2-7. Such a negative active material having no particular shape advantageously provides for a high capacity with a high yield (Applicants' specification, page 7, lines 9-18), which could not be achieved by producing carbonaceous material having a particular shape as required by Hayashi. Thus, Hayashi fails to teach or suggest all of the limitations of amended independent Claims 1, 3 and 5.

Accordingly, Applicants respectfully request withdrawal of the rejection of independent Claims 1, 3 and 5. Claims 2, 4, and 6-8 respectively depend from independent Claims 1, 3 and 5 and are not anticipated or obvious for at least the same reasons.

## II. Claims Rejected Under 35 U.S.C. § 103(a)

The Patent Office rejects Claims 5-8 under 35 U.S.C. 103(a) as being obvious over U.S. Patent No. 5,721,071 to Sonobe, et al. ("Sonobe"). Applicants respectfully traverse this rejection.

In maintaining the rejection, the Patent Office relies on Example 4 of Sonobe to show a petroleum pitch having a quinoline-insoluble content of 1 wt% that is heat treated at 600°C for one hour (coking) in a nitrogen gas stream. The pitch was then pulverized to obtain carbon precursor particles. The carbon precursor particles were carbonized and graphitized to obtain a graphitic material.

NO In response, Applicants submit that it is improper to conclude from the pitch content alone that Example 4 of Sonobe teaches the process steps of dissolving a petroleum pitch in a quinoline solvent and removing the insoluble components therefrom before heat treatment. Rather, it appears as though the petroleum pitch of Example 4 is a natural pitch without any pre-treatment (e.g., such as dissolving in an organic solvent). However, Applicants' independent Claim 5 specifically recites that the pitch is to be dissolved in an organic solvent to remove organic-insoluble components

therefrom and to obtain organic-soluble components. Subsequently, the organic-soluble components, having the organic-insoluble components removed, are heat treated as recited in Applicants' independent Claim 5. Thus, Sonobe fails to teach or suggest all of the limitations of independent Claim 5.

Accordingly, Applicants respectfully request withdrawal of the rejection of independent Claim 5. Claims 6-8 depend from independent Claim 5 and are not obvious at least for the same reasons.

**CONCLUSION**

In view of the foregoing, it is believed that all claims now pending (1) are in proper form, (2) are neither obvious nor anticipated by the relied upon art of record, and (3) are in condition for allowance. A Notice of Allowance is earnestly solicited at the earliest possible date. If the Examiner believes that a telephone conference would be useful in moving the application forward to allowance, the Examiner is encouraged to contact the undersigned at (310) 207-3800.

If necessary, the Commissioner is hereby authorized in this, concurrent and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2666 for any additional fees required under 37 C.F.R. §§ 1.16 or 1.17, particularly, extension of time fees.

Respectfully submitted,

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Dated: 9/24, 2002

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**CERTIFICATE OF TRANSMISSION:**

*I hereby certify that this paper is being facsimile transmitted to the U.S. Patent and Trademark Office on September 24, 2002.*

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September 24, 2002  
September 24, 2002

9-24-02

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE CLAIMS

Please amend the claims as follows:

1 1. (Four Times Amended) A negative active material for a lithium secondary battery,  
2 comprising a heat-treated graphite carbon material having no particular shape and an intensity ratio  
3  $I(110)/I(002)$  of an X-ray diffraction peak intensity  $I(002)$  at a (002) plane to an X-ray diffraction  
4 peak intensity  $I(110)$  at a (110) plane of less than 0.2, the negative active material prepared by  
5 dissolving a coal tar pitch or a petroleum pitch in an organic solvent to remove organic-  
6 insoluble components therefrom and to obtain organic-soluble components;  
7 heat-treating the organic-soluble components at a temperature in the range of 400 to 450 °C  
8 for 4 hours or more under an inert atmosphere to thereby produce at least 50 weight percent of  
9 mesophase particles based on the pitch;  
10 coking the pitch including mesophase particles;  
11 carbonizing the coked pitch;  
12 pulverizing the carbonized pitch; and  
13 graphitizing the pulverized pitch.

1 3. (Four Times Amended) A lithium secondary battery comprising:  
2 a negative electrode comprising a negative active material;  
3 a positive electrode comprising a lithium containing material that can reversibly intercalate  
4 and de-intercalate lithium ion; and  
5 a non-aqueous electrolyte;  
6 the negative active material comprising a heat-treated graphite carbon material having no  
7 particular shape and an intensity ratio  $I(110)/I(002)$  of an X-ray diffraction peak intensity  $I(002)$  at  
8 a (002) plane to an X-ray diffraction peak intensity  $I(110)$  at a (110) plane of less than 0.2 and the  
9 negative active material prepared by

dissolving a coal tar pitch or a petroleum pitch in an organic solvent to remove organic-  
 insoluble components therefrom and to obtain organic-soluble components;  
 heat-treating the organic-soluble components at a temperature in the range of 400 to 450 °C  
 for 4 hours or more under an inert atmosphere to thereby produce at least 50 weight percent of  
 mesophase particles based on the pitch;  
 coking the pitch including mesophase particles;  
 carbonizing the coked pitch;  
 pulverizing the carbonized pitch; and  
 graphitizing the pulverized pitch.

5. (Twice Amended) A method of preparing a negative active material having no  
particular shape for a lithium secondary battery, comprising the steps of:  
 dissolving a coal tar pitch or a petroleum pitch in an organic solvent to remove organic-  
 insoluble components therefrom and to obtain organic-soluble components;  
 heat-treating the organic-soluble components at a temperature in the range of 400 to 450 °C  
 for 4 hours or more under an inert atmosphere to thereby produce at least 50 weight percent of  
 mesophase particles having no particular shape based on the pitch;  
 coking the pitch including mesophase particles;  
 carbonizing the coked pitch;  
 pulverizing the carbonized pitch; and  
 graphitizing the pulverized pitch.

#14 (cont.)  
9.29.22  
Translation

[SPECIFICATION]

[TITLE OF THE INVENTION]

METHOD OF PREPARING NEGATIVE ACTIVE MATERIAL FOR  
LITHIUM SECONDARY BATTERY

5 [BRIEF DESCRIPTION OF THE DRAWINGS]

FIG. 1 is a schematic diagram of a 2016 typed coin cell; and

FIG. 2 is a schematic diagram of a 18650 typed cylindrical cell.

\* Reference Numeral Key of the Main Appearing in the Drawings \*

1: Positive collector	1": Negative collector	5: Can
10: Positive active material or counter electrode	15: Electrolyte	20: Gasket
25: Separator	30: Negative active material	35: Cap
50: Positive electrode	55: Negative electrode	60: Separator
65: Mandrill	70: Positive electrode lead	75: Negative electrode lead
80: Upper insulating plate	80' : lower insulating plating	85 : Can button

15 [DETAILED DESCRIPTION OF THE INVENTION]

[OBJECT OF THE INVENTION]

[DESCRIPTION OF THE RELATED ART]

[Field of the Invention]

20 The present invention relates to a method of preparing a negative active material for a lithium secondary battery, and more particularly, to a method of preparing a negative active material having a high capacity.

[Description of the Related Art]

In recent years, the development of miniaturized portable electronics provokes needs for a secondary battery having a high capacity as well as a light

weight, and from the viewpoint of the capacity improvement per unit weight, the lithium secondary battery is preferably adopted because lithium has a high standard potential as well as a low electrochemical equivalent weight. In general, cells are classified as follows: a primary cell, such as manganese  
5 battery, an alkali battery, a mercury battery and a silver oxide battery, which are not recharged electrically and hence are discarded after discharging; a secondary cell, such as a lead storage battery, a Ni-MH (nickel-metalhydride) battery using metal hydride as a negative active material, sealed nickel-cadmium battery, a lithium-metal battery, lithium ion battery (LIB), a lithium-  
10 polymer battery (LPB), which can be recharged electrically to their original condition after use; a fuel battery; and a solar battery.

The primary cell has a disadvantage in that the cell has a low capacity, a short lifetime and is not reused. On the other hand, the secondary cell has an advantage in that the cell has a long lifetime by recharging and reusing, and  
15 has a higher voltage than a primary cell so that the cell has a high performance and efficiency, and the cell can be reused.

Fig. 1 is a schematic cross sectional view showing the general structure of the coin-typed lithium secondary battery. As shown in Fig. 1, the lithium secondary battery includes a positive active material layer 10 on a collector 1  
20 made of nickel and a negative active material layer 30 on a collector 1' made of copper, a separator 25, a can 5, a cap 35 and a gasket 20. Fig. 2 is a schematic cross sectional view showing the general structure of the cylindrical-typed lithium secondary battery. As shown in Fig. 2, the lithium secondary battery includes positive electrodes 50, negative electrodes 55 stacked in order



and separated by a separator 60, a mandrill 65, a positive electrode lead 70, a negative electrode lead 75, upper insulating plate 80, lower insulating plate 80', and a can button 85, -

Lithium-containing transitional metal oxide such as  $\text{LiCoO}_2$ ,  $\text{LiNO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_y$  are preferably selected for the positive electrode active materials in conjugation with a polyethylene-based porous film for the separator. As for the negative electrode active materials, lithium metal is attractive because it has a light weight and high capacity per unit weight to thereby output high voltage in the battery use. However, the use of lithium metal for the negative electrode material reveals serious defects in a cycle life and stability of the battery because the lithium metal is highly reactive with the electrolytic solvent and easily forms needle dendrites during cycling, causing destruction of the separator and a short circuit. In order to avoid the defects, lithium alloys are employed as the negative electrode active material instead of the lithium metal but yet reveals similar problems.

Alternatively, carbon materials, which can reversibly accept and donate significant amounts of lithium without affecting their mechanical and electrical properties, are proposed for the negative electrode active material.

The carbon materials adapted for use in a battery are generally spherical type carbon materials and fiber type carbon materials. A method for preparing the spherical type carbon material is disclosed in Japanese Patent No. Hei 1-27968. In the method, a coal tar pitch is heat-treated and centrifuged to thereby produce small spherical particles having an optical anisotropy (referred to hereinafter more simply as mesophase particles). Alternatively, a coal tar

pitch is centrifuged to obtain supernatant and the supernatant is heat-treated, obtaining mesocarbon microbeads.

However, the aforementioned techniques are not economical and the manufacturing process is complicate because the centrifugation step should  
5 performed for obtaining mesophase particles. Furthermore, mesophase particles is only used for preparing spherical carbon materials, the total yield is low.

#### **[SUBJECT MATTER OF THE INVENTION]**

It is an object of the present invention to provide a method of preparing  
10 a negative active material for a lithium secondary battery having a high charge and discharge capacity, and efficiency.

It is another object of the present invention to provide a method of preparing the negative active material with simple manufacturing process and high yield.

#### **[ELEMENTS AND WORKING EXAMPLES OF THE INVENTION]**

##### **[Means for solving the subject]**

In order to achieve this object and others, the present invention provides a method of preparing a negative active material for a lithium secondary battery, including dissolving a coal tar pitch or a petroleum pitch in  
20 an organic solvent to remove insoluble components therefrom, heat-treating the pitch at a temperature in the range of 400 to 450 °C for four hours or more to thereby produce at least 50 weight percent of mesophase particles based on the pitch, coking the pitch including the mesophase particles, carbonizing the

coked pitch, pulverizing the carbonized pitch and graphitizing the pulverized pitch.

The present invention will be illustrated in more detail.

The negative active material is prepared by the following method.

5 A coal tar pitch or a petroleum pitch is dissolved in an organic solvent to remove insoluble components therefrom. The organic solvent may be tetrahydrofuran, quinoline, benzene or toluene. The pitch is heat-treated at a temperature in the range of 400 to 450 °C for 4 hours or more under an inert atmosphere such as nitrogen or argon to thereby produce at least 50 weight  
10 percent of mesophase particles based on the pitch. The mesophase particles contained in the pitch may present in the amount of 50 to 98 weight percent. The pitch including the 50 to 98 weight percent of mesophase particles is used for preparing negative active material, a battery having a high capacity can be produced. The pitch including the mesophase particles is coked. The coking  
15 step is preferably performed at a rising temperature up to 600 °C under an inert atmosphere. Thereafter, the coked pitch is carbonized at a temperature in the range of 1,000 to 1,300 °C. The carbonizing step is to remove components such as H, N and O from the coked material. The components are not well removed at temperatures lower than 1,000 °C. On the other hand, when the  
20 carbonizing step is performed at temperature exceeding 1,300 °C, a fine structure is significantly developed, causing reduction in the charge and discharge capacity. The carbonized pitch is pulverized to thereby produce no particular shape particles. The amorphous particles are graphitized at a

temperature in the range of 2,500 to 3,000 °C. The graphitizing step is to arrange the fine structure of the carbonized material. When the graphitizing step is performed at temperatures below 2,500 °C, the crystalline structure is not well developed and amorphous portions may be present. On the other  
6 hand, when the graphitizing step is performed at temperatures exceeding 3,000 °C, the charge and discharge capacity is undesirably low.

The present carbon material for used in the lithium secondary battery includes the mesophase particles in the optimum content. In the present invention, the optimum content is controlled by determining the electrochemical  
10 characteristics of the carbon material, while the mesophase particles content is changed. Conventionally, as the mesophase particles, spherical or fibrous mesophase particles are only used for preparing a negative active material. Due to this, the separation of spherical or fibrous mesophase particles should be performed, causing the complication of negative active material  
15 manufacturing process. Furthermore, as the no spherical or no fibrous mesophase particles wastes, the total yield is low. On the hand, in the present invention, the mesophase particles having no particular shape is used in the present invention without separating spherical mesophase particles or fibrous mesophase particles. Therefore, a negative active material having a high  
20 capacity can be produced with a high yield. The graphite-like carbon material for use in the present invention has a crystal size in the direction of the c axis (Lc) of 10-100 nm and in the direction of the a axis (La) of 20- 200 nm, and a specific surface of 3-20 m<sup>2</sup>/g.

The present invention will be now described with reference to Examples and drawings.

#### Example 1

A coal tar pitch was dissolved in tetrahydrofuran and insoluble  
5 components were removed therefrom. The residual components were heat-treated at 430 °C for four hours under a gaseous nitrogen atmosphere to thereby produce 50 weight percent of mesophase particles based on the pitch. Thereafter, the resulting pitch including mesophase particles were heated at a rising temperature up to 600 °C under a gaseous nitrogen atmosphere to  
10 thereby coke them. The coked pitch was then carbonized at 1000 °C. Next, the carbonized pitch was pulverized to thereby obtain a pulverized pitch having no particular shape. The pulverized pitch having no particular shape was graphitized at 2800 °C for 30 minutes under an inert atmosphere of gaseous nitrogen/argon atmosphere. As a result, a carbon material having a graphite  
15 structure was prepared.

The carbon material was mixed with a solution of polyvinylene fluoride in a N-methyl pyrrolidone solvent to be thereby made into a slurry. Then, the slurry was coated on a collector made of copper foil to thereby form a negative electrode plate. Next, a lithium secondary cell was as shown in Fig. 1  
20 prepared using the negative electrode plate together with a current electrode made of lithium metal foil and an electrolyte of  $\text{LiPF}_6$  in an organic solvent under an Ar inert gas. The capacity and discharge efficiency (discharge capacity/charge capacity) of each cell were measured and the results are presented in

Table 1.

## Example 2

A carbon material was prepared by the same procedure in Example 1 except that the tetrahydrofuran-insoluble components removed pitch was heat-treated at 430 °C for 8 hours to thereby produce 70 weight percent of mesophase particles base on the pitch.

The carbon material was mixed with a solution of polyvinylene fluoride in a N-methyl pyrrolidone solvent to be thereby made into a slurry. Then, the slurry was coated on a collector made of copper foil to thereby form a negative electrode plate. Next, a lithium secondary cell was as shown in Fig. 1 prepared using the negative electrode plate together with a current electrode made of lithium metal foil and an electrolyte of  $\text{LiPF}_6$  in an organic solvent under an Ar inert gas. The capacity and discharge efficiency (discharge capacity/charge capacity) of each cell were measured and the results are presented in Table 1.

## Example 3

A carbon material was prepared by the same procedure in Example 1 except that the tetrahydrofuran-insoluble components removed pitch was heat-treated at 430 °C for 15 hours to thereby produce 98 weight percent of mesophase particles base on the pitch.

The carbon material was mixed with a solution of polyvinylene fluoride in a N-methyl pyrrolidone solvent to be thereby made into a slurry. Then, the slurry was coated on a collector made of copper foil to thereby form a negative electrode plate. Next, a lithium secondary cell was as shown in Fig. 1

prepared using the negative electrode plate together with a current electrode made of lithium metal foil and an electrolyte of  $\text{LiPF}_6$  in an organic solvent under an Ar inert gas. The capacity and discharge efficiency (discharge capacity/charge capacity) of each cell were measured and the results are presented in

5 Table 1.

(Control 1)

For comparison, a polyvinylidene fluoride binder was dissolved in a N-methylpyrrolidone solvent and mesocarbon microbeads (Japan, Osaka Gas) was added to the resulting material thereby made into a slurry. Then, the  
10 slurry was coated on a collector made of copper foil to thereby form a negative electrode plate. Next, a lithium secondary cell was as shown in Fig. 1 prepared using the negative electrode plate together with a current electrode made of lithium metal foil under an Ar inert gas. The capacity and discharge efficiency of the compared cell was also measured and the results are  
15 presented in Table 1.

Table 1

	Capacity [mAh/g]	Efficiency
Example 1	290	88
Example 2	300	83
Example 3	314	92
Control 1	280	85

(Example 4)

For reference, a cylindrical cell as shown in Fig.2 was manufactured by

using a negative electrode plate including the carbon material obtained by the Example 3 coated on a current collector made of copper foil and a positive electrode plate including  $\text{LiCoO}_2$  coated on a collector made of the nickel foil. The capacity of the cylindrical cell was measured and the results are 1600 mAh.

5 **[Effect of the invention]**

As described above, in the present invention, the each of carbon materials having different mesophase particles content and is used for a lithium secondary battery, the lithium secondary battery having a high capacity can be prepared. Furthermore, the present invention can produce carbon material  
10 with a simple manufacturing process and a high yield.



**[WHAT IS CLAIMED IS:]**

1. A method of preparing a negative active material for a lithium secondary battery, comprising the steps of:

dissolving a coar tar pitch or a petroleum pitch in an organic solvent to  
5 remove insoluble components therefrom;

heat-treating the pitch at a temperature in the range of 400 to 450 °C  
for 4 hours or more under an inert atmosphere to thereby produce at least 50  
weight percent of mesophase particles based on the pitch;

coking the pitch including mesophase particles;

10 carbonizing the coked pitch;

pulverizing the carbonized pitch; and

graphitizing the pulverized pitch.

2. The method of claim 1 wherein the inert atmosphere is a gaseous nitrogen or argon atmosphere.

15 3. The method of claim 1 wherein the mesophase particles are produced by 50 to 98 weight percent based on the pitch.

4. The method of claim 1 wherein the coking step is performed at a rising temperature up to 600 °C under an inert atmosphere.

20 5. The method of claim 1 wherein the carbonizing step is performed at 900°C or more.

6. The method of claim 1 wherein the graphitizing step is performed at 2000°C or more.

**FIG**

Omitted

KOREAN INDUSTRIAL PROPERTY OFFICE

This is to certify that the following application annexed hereto is a true copy from the records of the Korean Industrial Property Office.

Application Number: Patent Application No. 1998-7854

Filing date: March 10, 1998

Applicant(s): Samsung Display Devices Co., Ltd.

This 16th day of April, 1998

COMMISSIONER

**[ABSTRACT OF THE DISCLOSURE]****[Abstract]**

A method of preparing a negative active material for a lithium secondary battery includes dissolving a coar tar pitch or a petroleum pitch in an organic solvent to remove insoluble components therefrom, heat-treating the pitch at a temperature in the range of 400 to 450 °C for 4 hours or more under an inert atmosphere to thereby produce at least 50 weight percent of mesophase particles based on the pitch, coking the pitch including mesophase particles, carbonizing the coked pitch, pulverizing the carbonized pitch; and graphitizing the pulverized pitch.

**[REPRESENTATIVE DRAWING]**

Fig. 1

(Translation)

**APPLICATION FOR PATENT**

Application Number : 10-1998-7854

Filing date : March 10, 1998

**TITLE OF INVENTION: METHOD OF PREPARING NEGATIVE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY**

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Submitted herewith is/are an application identified above pursuant to Article 42 of the Patent Act.

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To the Commissioner of  
the Korean Industrial Property Office

Attachment: 1. Copy application form, specification, claims,  
abstract and drawings

I, the undersigned, who have prepared English translation which is attached herewith, hereby declare that the aforementioned translation is true and correct translation of officially certified copy of the Korean Patent Application No. 98-7854 filed on March 10, 1998.

This 19th day of September, 2002

Translator:

  
Hyo-Jin Kim